

R. McCURDY
Appln. No. 09/662,181
Amendment Under 37 C.F.R. § 1.114(c)

LISTING OF CLAIMS:

Claims 1-32 (canceled).

33. (previously presented): A method comprising the steps of:
manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath, positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the temperature is from about 590° to 715°C (1100° to 1320°F);

directing titanium tetrachloride in a carrier gas stream through said chemical vapor deposition apparatus over a surface of the float ribbon and annealing the float ribbon to produce titanium dioxide in the crystalline phase as a photocatalytically-activated self-cleaning coating over the glass float ribbon.

34. (previously presented): The method of claim 33 wherein the directing of the metal oxide precursor is directly onto the surface of the float ribbon without any intervening coating layers.

35. (previously presented): A method comprising the steps of:
manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath;

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depositing a coating over at least one of the major surfaces by positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the temperature range is from about 590° to 715°C (1100° to 1320°F), directing a precursor gas mixture comprising titanium tetrachloride and an organic oxygen containing compound, wherein the concentration of the titanium tetrachloride is in the range from about 0.1-5.0 % by volume, through said chemical vapor deposition coating apparatus over a surface of the float ribbon and annealing the float ribbon in air to produce titanium dioxide in the crystalline phase as a photocatalytically-activated self-cleaning coating over the glass float ribbon.

36. (previously presented): The method of claim 35 wherein the directing of the metal oxide precursor is directly onto the surface of the float ribbon without any intervening coating layers.

37. (previously presented): In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

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depositing by chemical vapor deposition a crystalline phase of a photocatalytically-activated self-cleaning titanium dioxide coating over a surface of said float ribbon as the float ribbon is formed.

38. (previously presented): The method of claim 37 the improvement further comprising: depositing a silica coating over a surface of said float ribbon and depositing said titanium dioxide coating over said silica coating.

39. (previously presented): The method of claim 38 wherein said titanium dioxide coating has a thickness of 1300Å.

40. (previously presented): The method of claim 37, the improvement further comprising: depositing a silica layer over a surface of said float ribbon and depositing said photocatalytically-activated self-cleaning coating over said silica layer wherein the thickness of the silica layer is about 339Å.

41. (previously presented): A method comprising steps of:
providing a glass article having at least one surface by a float manufacturing process;
depositing a photocatalytically-activated self-cleaning coating over the surface of the article by chemical vapor deposition during the glass manufacturing process so that the coating has titanium dioxide in the crystalline phase and has a thickness of 1300Å.

42. (previously presented): A method comprising the steps of:
providing an article of manufacture having at least one surface;
depositing a silica layer by chemical vapor deposition having a thickness of about 339Å over said surface; and

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depositing a photocatalytically-activated self-cleaning coating by chemical vapor deposition over said silica layer whereupon said silica layer inhibits migration of sodium ions from the surface of said article to said photocatalytically-activated self-cleaning coating.

43. (canceled).

44. (previously presented): The method of claim 42 wherein the article is selected from the group consisting of: glass sheet and continuous glass float ribbon.

45-46. (canceled).

47. (previously presented): A method comprising the steps of:
manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath, positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the temperature range is from about 590° to 715°C (1100° to 1320°F);

directing titanium tetrachloride in a carrier gas stream through said chemical vapor deposition apparatus over a surface of the float ribbon and annealing the float ribbon to produce titanium dioxide in the crystalline phase as a photocatalytically-activated self-cleaning coating over the glass float ribbon whereby said coating has a photocatalytically activated self-cleaning reaction rate of 8.1×10^{-3} to $9.1 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$.

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48. (previously presented): The method of claim 47 wherein the directing of the metal oxide precursor is directly onto the surface of the float ribbon without any intervening coating layers.

49. (previously presented): A method comprising the steps of:
manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath;
depositing a coating over at least one of the major surfaces by positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the temperature range is from about 590° to 715°C (1100° to 1320°F), directing a precursor gas mixture comprising titanium tetrachloride and an organic oxygen containing compound, wherein the concentration of the titanium tetrachloride is in the range from about 0.1-5.0% by volume, through said chemical vapor deposition coating apparatus over a surface of the float ribbon and annealing the float ribbon to produce titanium dioxide in the crystalline phase as a photocatalytically-activated self-cleaning coating over the glass float ribbon whereby said coating has a photocatalytically activated self-cleaning reaction rate of 8.1×10^{-3} to $9.1 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$.

50. (previously presented): The method of claim 49 wherein the directing of the metal oxide precursor is directly onto the surface of the float ribbon without any intervening coating layers.

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51. (previously presented): In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing by chemical vapor deposition a crystalline phase of a photocatalytically-activated self-cleaning titanium dioxide coating over a surface of said float ribbon as the float ribbon is formed whereby said coating has a photocatalytically-activated self-cleaning reaction rate of 8.1×10^{-3} to $9.1 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$.

52. (previously presented): The method of claim 51 the improvement further comprising: depositing a silica coating over a surface of said float ribbon and depositing said titanium dioxide coating over said silica coating.

53. (previously presented): The method of claim 52 wherein said titanium dioxide coating has a thickness of 1300Å.

54. (previously presented): The method of claim 51, the improvement further comprising: depositing a silica layer over a surface of said float ribbon and depositing said photocatalytically-activated self-cleaning coating over said silica layer wherein the thickness of the silica layer is about 339Å.

55. (previously presented): A method comprising steps of:

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providing a glass article having at least one surface by a float manufacturing process;
depositing a photocatalytically-activated self-cleaning coating over the surface of the article by chemical vapor deposition during the glass manufacturing process so that the coating has titanium dioxide in the crystalline phase and has a thickness of 1300Å whereby said coating has a photocatalytically-activated self-cleaning reaction rate of 8.1×10^{-3} to $9.1 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$.

56. (withdrawn): A method for hydrophilifying the surface of a substrates comprising the steps of:

providing a substrate coated with a solid layer having an interface with air, and containing a photocatalyst; and
photoexciting the photocatalyst to permit molecules of water to be physically adsorbed onto the surface of said layer under the photocatalytic action of said photocatalyst, thereby hydrophilifying the surface of said substrate.

57. (withdrawn): A method for hydrophilifying the surface of a substrate, comprising the steps of:

providing a substrate coated with a solid layer having an interface with air, said layer containing a photocatalyst, and, at said interface, a hydrogen bond component, γ_s^h ; and
photoexciting the photocatalyst to increase said hydrogen bond component under the photocatalytic action of said photocatalyst.

58. (withdrawn): A method for hydrophilifying the surface of a substrate, comprising the steps of:

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providing a substrate coated with a solid layer having an interface with air, said layer containing a photocatalyst, and having, at said interface, a hydrogen bond component, γ_s^h ; and photoexciting the photocatalyst to increase said hydrogen bond component under the photocatalytic action of said photocatalyst, thereby accelerating the physical adsorption of molecules of water onto the surface of said layer.

59. (withdrawn): A method for enhancing the oil repellency of the surface of a substrate in water, comprising the steps of:

providing a substrate coated with a solid layer having an interface with air, and containing a photocatalyst; and
photoexciting the photocatalyst to increase a hydrogen bond component, in the surface energy in the solid/gas interface of said layer under the photocatalytic action of said photocatalyst, thereby enhancing the oil repellency of the surface of the substrate when placed in water.

60. (withdrawn): A method for cleaning a substrate, comprising the steps of:
providing a substrate coated with a solid layer having an interface with air, and containing a photocatalytic semiconductor material;
photoexciting the photocatalyst to enhance a hydrogen bond component, γ_s^h , in the surface energy in the solid/gas interface of said layer under the photocatalytic action of said photocatalyst, thereby enhancing the oil repellency of the surface of the substrate when placed in water; and

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immersing the substrate in water or wetting the substrate with water to release an oil stain adhering on the surface of the substrate.

61. (withdrawn): A composite with a hydrophilifiable surface, comprising:
a substrate;
a solid layer provided on the surface of the substrate and having an interface with air, said layer containing a photocatalyst; and
a layer of molecules of water physically adsorbed onto the surface of said layer containing a photocatalyst in response to the photoexcitation of the photocatalyst.

62. (withdrawn): A composite with a hydrophilifiable surface, comprising:
a substrate; and
a solid layer provided on the surface of the substrate and having an interface with air, said layer containing a photocatalyst and adapted to increase the hydrogen bond component, γ_s^h , in the surface energy at said interface in response to the photoexcitation of said photocatalyst.

63. (withdrawn): A composite with a hydrophilifiable surface, comprising:
a substrate;
a solid layer provided on the surface of the substrate and having an interface with air, said layer containing a photocatalyst and adapted to increase the hydrogen bond component, γ_s^h , in the surface energy at said interface in response to photoexcitation of said photocatalyst; and
a layer of molecules of water physically adsorbed onto the surface of said layer containing a photocatalyst in response to the photoexcitation of the photocatalyst.

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64. (withdrawn): A composite with a surface adapted to be rendered oil repellent in water, comprising:

a substrate;
a solid layer provided on the surface of the substrate and having an interface with air, said layer containing a photocatalyst and adapted to increase the hydrogen bond component, γ_s^h , in the surface energy at said interface in response to photoexcitation of said photocatalyst, thereby increasing the oil repellency of the surface of the composite in water.

65. (withdrawn): A composite with an easily cleanable surface, comprising:
a substrate; and
a solid layer provided on the surface of the substrate and having an interface with air, said layer containing a photocatalyst,
said layer operating to increase the hydrogen bond component, γ_s^h , in the surface energy at said interface in response to photoexcitation of the photocatalyst, thereby enhancing the oil repellency of the surface of the composite in water, whereby, upon immersion of the composite in water or wetting of the composite with water, an oil stain adhering on the surface of said layer is released therefrom.

66. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and obtained by thermal decomposition of titanium tetrachloride precursors, wherein said coating has a thickness up to

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130 nm and wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 0.5 and 60 nm.

67. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces with a coating having a photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and a thin layer forming a barrier to alkali metals originating from the substrate, located between said substrate and said coating, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 0.5 and 60 nm.

68. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein said coating is hydrophilic, and has a contact angle with water below 5° after exposure to luminous rays, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 0.5 and 60 nm.

69. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein said coating has a root mean square (RMS) rugosity between 2 and 20 nm, wherein the crystallized titanium oxide is in the form of crystallites with an average size of between 0.5 and 60 nm.

70. (withdrawn): The coated substrate according to claim 67, wherein the coating has a thickness up to 130 nm.

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71. (withdrawn): The coated substrate according to claim 68, wherein the coating has a thickness of up to 130 nm.

72. (withdrawn): The coated substrate according to claim 69, wherein the coating has a thickness up to 130 nm.

73. (withdrawn): The coated substrate according to claim 67, wherein the thin layer comprises silicon or silica.

74. (withdrawn): A multi-layer glazing wherein at least one layer thereof is the coated substrate of claim 66.

75. (withdrawn): A multi-layer glazing wherein at least one layer thereof is the coated substrate of claim 67.

76. (withdrawn): A multi-layer glazing wherein at least one layer thereof is the coated substrate of claim 68.

77. (withdrawn): A multi-layer glazing wherein at least one layer thereof is the coated substrate of claim 69.

78. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and obtained by chemical vapor deposition followed by an annealing heat treatment.

79. (withdrawn): The coated substrate according to claim 1, wherein the coating has a thickness up to 130 nm.

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80. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein at least one thin layer is located between said substrate and said coating.

81. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces, and contacting said portion, with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form.

82. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces, with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein an underlayer is present between, and contacts, said substrate and said coating, and which underlayer acts as a barrier with respect to alkali ions.

83. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces, with a coating having photocatalytic properties, and comprising regions of titanium oxide at least partly crystallized in the anatase form and regions of an amorphous or partially crystalline oxide of titanium other than anatase form.

84. (withdrawn): A double glass glazing comprising on at least a portion of one of its outer faces a coating having photocatalytic properties, wherein said coating comprises titanium oxide at least partly crystallized in the anatase form.

85. (withdrawn): A coated substrate which is a glass substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising

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titanium oxide at least partly crystallized in the anatase form, wherein the crystallized titanium oxide is in the form of crystallites, and the thickness of the coating is at least two times greater than the mean diameter of said crystallites.

86. (withdrawn): The coated substrate of claim 85, wherein the crystallites have an average size between 0.5 and 100 nm.

87. (withdrawn): A titanium dioxide photocatalyst structure comprising:
a transparent glass substrate having first and second opposing surfaces, said transparent glass substrate containing alkaline ingredients therein, the first surface of said substrate receiving light from an external light source;

a titanium dioxide film having first and second opposing surfaces, a light transmittance of said titanium dioxide film being at least 50% for light having a wavelength of 550 nm, the first surface of said titanium dioxide film being formed on the second surface of said substrate, whereby light transmitted from said external source through the first and second opposing surfaces of said substrate and through the first surface of said titanium dioxide film to the second surface thereof causes photocatalytic activity to be generated on the second surface of said titanium dioxide film; and

a transparent precoat film interposed between the second surface of said substrate and the first surface of said titanium dioxide film.

88. (withdrawn): The titanium dioxide photocatalyst structure according to claim 87, wherein said transparent precoat film has a thickness of 0.02 μm to 0.2 μm .

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89. (withdrawn): The titanium dioxide photocatalyst structure according to claim 88, wherein said precoat film is composed of SiO₂.

90. (withdrawn): A titanium dioxide photocatalyst structure comprising:
a transparent substrate;
a titanium dioxide film formed on said substrate, said titanium dioxide film having photocatalytic activity and a light transmittance of at least 50% for light having a wavelength of 550 nm; and
a transparent precoat film disposed between the transparent substrate and the titanium dioxide film.

91. (withdrawn): The titanium dioxide photocatalyst structure according to claim 90 wherein the precoat film has a thickness of 0.02 μm to 0.2 μm.

92. (withdrawn): The titanium dioxide photocatalyst structure according to claim 90 wherein the precoat film is composed of SiO₂.

93. (withdrawn): A method for producing a titanium dioxide photocatalyst structure according to claim 90 comprising a producing process which includes the step of forming the titanium dioxide film on the transparent substrate by a method selected from the group consisting of a pyro-sol method, a dipping method, a printing method and a CVD method.

94. (withdrawn): A titanium dioxide photocatalyst structure comprising:
a transparent substrate;

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a titanium dioxide film formed on said substrate, said titanium dioxide film having a thickness of 0.1 μm to 5 μm , photocatalytic activity and a light transmittance of at least 50% for light having a wavelength of 550 nm; and

a transparent precoat film disposed between the transparent substrate and the titanium dioxide film.

95. (withdrawn): The titanium dioxide photocatalyst structure according to claim 94 wherein the precoat film has a thickness of 0.02 μm to 0.2 μm .

96. (withdrawn): The titanium dioxide photocatalyst structure according to claim 94 wherein the precoat film is composed of SiO_2 .

97. (withdrawn): A titanium dioxide photocatalyst structure comprising:
a transparent substrate;
a titanium dioxide film, containing an anatase crystal, formed on said substrate, said titanium dioxide film having photocatalytic activity and a light transmittance of at least 50% for light having a wavelength of 550 nm; and

a transparent precoat film disposed between the transparent substrate and the titanium dioxide film.

98. (withdrawn): The titanium dioxide photocatalyst structure according to claim 97 wherein the precoat film has a thickness of 0.02 μm to 0.2 μm .

99. (withdrawn): The titanium dioxide photocatalyst structure according to claim 97 wherein the precoat film is composed of SiO_2 .